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On the foundations of the linear theory of irreversible processes. I

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1. Introduction

The purpose of this and a subsequent paper is a study of the linear phenomenological theory of irreversible processes with emphasis on its logical structure, its possible probabilistic interpretation, and its relation to statistical mechanics, that is to microscopic dynamics. We shall restrict ourselves to systems which can be characterized by a finite number of thermodynamic coordinates, the kinetics of the system being determined by a set of linear phenomenological equations. The thermodynamic coordinates are not assumed to have the same parity with respect to a reversion of the direction of the microscopic motion and time reversal is introduced into the theory as a linear involutory operation on the thermodynamic coordinates.

Particular interest is devoted to the question of irreversibility. It is pointed out that for an arbitrary system of the type considered any initial thermodynamic state may be considered as a linear superposition of two states one giving rise to strictly irreversible processes and the other to strictly reversible processes. The decomposition is unique and very closely related to the possible probabilistic interpretation of the theory. It will turn out that reversible processes correspond to random processes which are of the so called deterministic type whereas irreversible processes correspond to random processes which are classified as non deterministic or purely random. This connection which is also strongly related to the question of macroscopic causality will be discussed in the second part of the present work.

For open systems, under the influence of external constraints which in general are time dependent, it is possible to introduce dissipation functions which depend only on the state of the system. These functions decrease monotonically in the course of time and characterize the approach of the system to a state (in general time dependent) which is determined by the external constraints and is independent of the initial state of the system. If in particular the external constraints are time independent, the final state of the system will thus be stationary. For systems which obey the principle of detailed balance, that is which are described by thermodynamic coordinates which are invariant under time reversal, a possible dissipation function is the entropy production. This fact is well known as Prigogine's theorem. On the other hand neither detailed balance nor the more general time reversal symmetry is essential for the existence of dissipation functions.

2. Outline of the phenomenological linear theory of irreversible processes

Let us consider a closed, adiabatically insulated system under fixed external conditions. We shall be concerned only with states of the system which are characterized by the values of a finite number of extensive variables $A = (A^1, \dots, A^n)$. We are thinking of a description of the system in terms of thermodynamic states, as outlined in [Uhlhorn, 1960 a]. The statement $A(t) = \alpha = (\alpha^1, \dots, \alpha^n)$ means that at the time t, the state of the system can be identified with a possible thermodynamic state corresponding to a particular constraint chosen from a given class of constraints. The particular constraint is determined by the value α and conversely the class of constraints determines the possible values of $A(t)$. The validity of such a description will not be discussed here.

There is no further restriction in the assumption that the prescribed constraint, that is the statement that the system be closed, adiabatically insulated etc., is expressed in terms of the $n-m$ extensive variables $A^{m+1}(t), \dots, A^n(t)$ in the form

$$A^\mu(t) = \mathring{\alpha}^\mu \qquad (\mu = m+1, \dots, n) \text{ for every time } t. \tag{1}$$

This can always be achieved by a proper linear transformation of the extensive variables.

We shall assume that under the prescribed constraint (1) the system has exactly one thermodynamic (equilibrium) state

$$A^\mu = \mathring{\alpha}^\mu \qquad (\mu = 1, \dots, m). \tag{2}$$

The state (2), when once produced, will persist as long as the constraint (1) is not changed. This means that if we observe the system, keeping the constraint (1) fixed, we will either find that the system ultimately reaches the state (2) and no further changes of its state will occur, or no stationary state is reached at all.

It is convenient to normalize the free variables A^μ to zero in the equiblibrium state (2). Thus in the following we take $\mathring{\alpha}^\mu = 0$ $(\mu = 1, \dots, m)$.

We shall assume that the free variables $A^1, \dots, A^m$ have a definite behaviour under time reversal, or more properly reversal of the direction of motion. We shall find it convenient to express this behaviour in terms of a linear transformation

$$T^\mu_\nu \, \alpha^\nu,^1 \tag{3}$$

which is involutory

$$T^\lambda_\mu \, T^\mu_\nu = \delta^\lambda_\nu. \tag{4}$$

For the given situation, the relevant thermodynamic potential is the, possibly generalized, entropy S, which considered as a function $S(\alpha)$ of the free variables has a proper maximum in the equilibrium state (2). Defining $s_{\mu\nu}$ by

$$s_{\mu\nu} \equiv -\frac{\partial^2 S}{\partial \alpha^\mu \, \partial \alpha^\nu}(0), \tag{5}$$

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[1] In the rest of this paragraph the indices ι, λ, μ, ν can take the values $1, \dots, m$. Summation convention is assumed for pairs of equal upper and lower indices.

we have the Taylor expansion, valid for small $|\alpha| = \sum_{\mu=1}^{\mu=m} |\alpha^\mu|$,

$$S(\alpha) = S(0) - \tfrac{1}{2} s_{\mu\nu} \alpha^\mu \alpha^\nu + o(|\alpha|^2). \tag{6}$$

The quadratic form $s_{\mu\nu} \alpha^\mu \alpha^\nu$ is positive definite:

$$\alpha \neq 0 \text{ implies } s_{\mu\nu} \alpha^\mu \alpha^\nu > 0. \tag{7}$$

The entropy function $S(\alpha)$ is invariant under time reversal (3) of its argument, and hence

$$T^\mu_\iota T^\nu_\lambda s_{\mu\nu} = s_{\iota\lambda}. \tag{8}$$

The thermodynamic forces ξ_μ corresponding to the thermodynamic coordinates α^μ are defined by

$$\xi_\mu = -s_{\mu\nu} \alpha^\nu. \tag{9}$$

According to (6)

$$\xi_\mu = \frac{\partial S(\alpha)}{\partial \alpha^\mu} + o(|\alpha|). \tag{10}$$

We observe that the connection between the variables α^μ and ξ_μ (9) is reversible and that both vanish only in the equilibrium state.

The phenomenological equations, which determine the time development of the system are conventionally written in the form (see e.g. [Onsager and Machlup, 1953]),

$$\frac{d}{dt} \alpha^\mu(t) = L^{\mu\nu} \xi_\nu(t). \tag{11}$$

The phenomenological coefficients are independent of time. They have the following three properties. The transformation $L^{\mu\nu} \xi_\nu$ is non singular, that is

$$L^{\mu\nu} \xi_\nu = 0 \text{ if and only if } \xi = 0. \tag{12}$$

This is equivalent to the assumed uniqueness of the equilibrium state. Further the quadratic form $L^{\mu\nu} \xi_\mu \xi_\nu$ is non negative, but not necessarily positive

$$L^{\mu\nu} \xi_\mu \xi_\nu = \tfrac{1}{2} (L^{\mu\nu} + L^{\nu\mu}) \xi_\mu \xi_\nu \geqslant 0. \tag{13}$$

This is a consequence of the fact that under the given constraints the entropy cannot decrease in the course of time

$$\frac{d}{dt} S[\alpha(t)] = \frac{\partial S}{\partial \alpha^\mu} \frac{d\alpha^\mu}{dt} = [\xi_\mu + o(|\alpha|)] L^{\mu\nu} \xi_\nu = L^{\mu\nu} \xi_\mu \xi_\nu + o(|\xi|^2) \geqslant 0. \tag{14}$$

Conventionally the quadratic expression (13) is called the entropy production in the state determined by ξ. The third property of the phenomenological coefficients is given by the Onsager reciprocal relations

$$T^{\lambda}_{\mu} L^{\mu\nu} = T^{\nu}_{\mu} L^{\mu\lambda}. \tag{15}$$

We observe that the linear phenomenological theory as formulated above is invariant under arbitrary non singular linear transformations of the thermodynamic coordinates. No metric concepts have been introduced so far. However, the theory contains two scalar invariants, the quadratic forms corresponding to the entropy and to the entropy production respectively. The quadratic form corresponding to the entropy is non singular and may be used to define a "natural" scalar product. Though there is no ambiguity in doing so, we shall find it more convenient to use the representation described below.

3. Representation of the linear theory

In order to get a clear insight into the logical structure of the linear theory of irreversible processes we shall introduce a representation of the theory in terms of a space V of "state vectors". Though the physical theory contains only real quantities we shall find it mathematically convenient to use a complex vector space for its representation. It will turn out that the algebraic structure of the linear theory also gives a very strong indication with respect to its possible statistical interpretation.

Let V be an m-dimensional complex vector space of elements $u, v, w, \dots$ with a Hermitian scalar product $(u\,|\,v)$, linear in its right argument and antilinear in its left argument. The norm of a vector v is defined by $\|v\| = (v\,|\,v)^{\frac{1}{2}}$. Let the space V be spanned by m vectors $u^1, \dots, u^m$ chosen so that their mutual scalar products are real, that is

$$(u^{\mu}\,|\,u^{\nu}) = (u^{\nu}\,|\,u^{\mu}).^{1} \tag{16}$$

The reciprocal basis $u_1, \dots, u_m$ is uniquely determined by the relations

$$(u^{\mu}\,|\,u_{\nu}) = \delta^{\mu}_{\nu}. \tag{17}$$

It is an evident consequence of (16) that

$$(u_{\mu}\,|\,u_{\nu}) = (u_{\nu}\,|\,u_{\mu}). \tag{18}$$

Complex conjugation of an arbitrary vector $v = u^{\mu}\,(u_{\mu}\,|\,v) = u_{\mu}\,(u^{\mu}\,|\,v)$ is defined by

$$C\,v = u^{\mu}\,\overline{(u_{\mu}\,|\,v)} = u^{\mu}\,(v\,|\,u_{\mu}). \tag{19}$$

According to its definition complex conjugation is an antilinear operation on V which leaves the norm invariant.

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[1] In this paragraph the indices μ, ν can take the values $1, \dots, m$; summation convention is assumed for pairs of equal upper and lower indices.

Let the linear operators s, T, L, M, and $Q(t)$ in V be defined by

$$\begin{aligned} s &= |u^{\mu})\, s_{\mu\nu}\, (u^{\nu}| \\ T &= |u_{\mu})\, T^{\mu}_{\nu}\, (u^{\nu}| \\ L &= |u_{\mu})\, L^{\mu\nu}\, (u_{\nu}| \\ M &= L\, s \\ Q(t) &= \exp\{-t M\} \qquad (t \geqslant 0). \end{aligned} \tag{20}$$

We shall call s the entropy operator, T the time reversal operator, and $Q(t)$ the semi-group generated by the phenomenological equations (11), for evidently $Q(t)$ has the semi-group property

$$Q(t_1)\, Q(t_2) = Q(t_1 + t_2)\; (t_1,\, t_2 \geqslant 0). \tag{21}$$

Further $Q(t)$ satisfies the initial condition $Q(0) = 1$. Its infinitesimal generator is $M = L s$. The operators (20) are real in the sense that they commute with the complex conjugation operation C.

It follows from (5) and (7) that the operator s is positive definite:

$$v \in V,\; v \neq 0 \;\text{ implies }\; (v\,|\,s\,|\,v) > 0, \tag{22}$$

and hence s^{-1}, the inverse of s, is well defined.

The time reversal operator T has according to (4) the involutory property, and is related to s by (8). The operator form of these relations is

$$T\,T = 1, \qquad (s\,T)^* = s\,T, \tag{23}$$

where * denotes Hermitian adjoint.

The Osager reciprocal relations (15) can be expressed in the form

$$(T\,L)^* = T\,L, \tag{24}$$

or equivalently as a condition on the operator M

$$M^* = (s\,T)\, M\, (s\,T)^{-1}, \tag{25}$$

that is, M and its Hermitian adjoint M^* are connected by a similarity transformation.

We shall now turn our interest to the phenomenological equations (11) or alternatively to the semi-group of linear transformations determined by $Q(t)$. In particular we shall determine the behaviour of $Q(t)$ for large values of t. Particular attention will be paid to the question whether the time reversal symmetry expressed by (25) represents a real restriction of the mathematical form of the phenomenological theory or not. As can be expected the time reversal symmetry will not simplify the mathematical treatment except for the particular cases in which T can be represented by 1 or -1, that is if the variables are all of the same kind with respect to reversion of the direction of motion.

Let us first recollect the properties we have assumed M to possess:

$$\begin{aligned} &\text{a. Non negative entropy production:}^{1}\ s^{-1} M^* + M s^{-1} \geqslant 0 \\ &\quad\ \text{(equivalently } M^* s + s M \geqslant 0) \\ &\text{b. Reality: } C M = M C \\ &\text{c. Onsager's relations: } M^* = (s T) M (s T)^{-1} \\ &\text{d. Non singularity: } M v = 0 \text{ implies } v = 0. \end{aligned} \tag{26}$$

To begin with we shall assume only the property a.. This property can also be given the form

$$Q(t)^* s Q(t) \equiv s(t) \leqslant s. \tag{27}$$

We recall that according to the definition (21) the operator $Q(t)$ is a solution of the phenomenological equations, with the initial condition $Q(0) = 1$. The inequality is an immediate consequence of the fact that $s(0) = s$ and that the derivative of $s(t)$ is

$$\frac{d}{dt} s(t) = -Q(t)^* [M^* s + s M] Q(t) \leqslant 0. \tag{28}$$

The meaning of (27) is of course that for an arbitrary vector v in V

$$\| s^{\frac{1}{2}} Q(t) v \|^2 \equiv (v \mid Q(t)^* s Q(t) \mid v) \leqslant (v \mid s \mid v) \equiv \| s^{\frac{1}{2}} v \|^2, \tag{29}$$

which is a statement of the fact that for an arbitrary initial state v the phenomenological equations (11) cause no decrease of the second order entropy. It follows further from (28) that the decrease of $s(t)$ with increasing t is monotonic. On the other hand $s(t)$ is a non negative operator and hence the limit

$$s(\infty) = \lim_{t \to \infty} s(t) \tag{30}$$

is a well defined non negative operator. It is evident that $s(\infty)$ is invariant under $Q(t)$:

$$Q(t)^* s(\infty) Q(t) = s(\infty), \tag{31}$$

or equivalently

$$M^* s(\infty) + s(\infty) M = 0. \tag{32}$$

It follows from (29) that

$$\lim_{t \to \infty} \| s^{\frac{1}{2}} Q(t) v \| = \| s(\infty)^{\frac{1}{2}} v \|. \tag{33}$$

Hence we find that

$$\lim_{t \to \infty} Q(t) v = 0 \text{ if and only if } s(\infty) v = 0,$$

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[1] An inequality of the form $A \geqslant B$ relating two linear operators in V has the meaning that $A - B$ is non negative, that is for any $v \in V$ $(v \mid A - B \mid v) \geqslant 0$.

that is, the system can reach equilibrium when started in an initial state v if and only if the vector v is an eigenvector of $s(\infty)$ corresponding to the eigenvalue 0.

Let the distinct eigenvalues of M be $\mu_1, \ldots, \mu_k$ and the corresponding multiplicities $m_1, \ldots, m_k$ $\left(\sum_{j=1}^{j=k} m_j = m\right)$. It is wellknown that the vector space V can be decomposed into a direct sum of k subspaces $V_1, \ldots, V_k$, of respective dimensions $m_1, \ldots, m_k$, such that each V_j is invariant under M and such that $(M-\mu_j)$ is nilpotent on V_j.[1] The subspaces are in general not mutually orthogonal. Taking the initial state v in V_j we have identically

$$Q(t)\,v = \exp\{-t\,\mu_j\}\exp\{-t\,[M-\mu_j]\}\,v = \exp\{-t\,\mu_j\}\,\pi_j([M-\mu_j]\,t)\,v. \qquad (34)$$

Here $\pi_j(\cdot)$ denotes a polonomial of degree less than or equal to m_j. From (34) we obtain easily some conditions which are necessary for the existence of the limit (30). We omit the proofs.

$$\begin{aligned}
&(a)\quad \mathrm{Re}\,(\mu_j) \geqslant 0.\\
&(b)\quad \mathrm{Re}\,(\mu_j) > 0 \text{ if and only if for every } v \in V_j,\, s(\infty)\,v = 0 \text{ or if and only if for every } v \in V_j,\ \lim_{t\to\infty} Q(t)\,v = 0.\\
&(c)\quad \text{If } \mathrm{Re}\,(\mu_j) = 0 \text{ and } v, w \in V_j: \quad (v\,|\,s(t)\,|\,w) = (v\,|\,s(\infty)\,|\,w) = (v\,|\,s\,|\,w).\\
&(d)\quad \text{If } \mathrm{Re}\,(\mu_i) = \mathrm{Re}\,(\mu_j) = 0,\ \mu_i \neq \mu_j \text{ and } v \in V_i,\ w \in V_j: \quad (v\,|\,s(t)\,|\,w) = (v\,|\,s(\infty)\,|\,w) = (v\,|\,s\,|\,w) = 0.
\end{aligned} \qquad (35)$$

Let W_0 denote the direct sum of the subspaces V_j with $\mathrm{Re}\,(\mu_j) > 0$ and W_I the direct sum of the subspaces V_j with $\mathrm{Re}\,(\mu_j) = 0$. Then V is the direct sum of W_0 and W_I and these subspaces are both invariant under M. The unique decomposition of an arbitrary vector $w \in V$

$$w = w_0 + w_I \qquad (w_0 \in W_0,\ w_I \in W_I) \qquad (36)$$

is in general not a decomposition into orthogonal components. Thus the corresponding projections P_0 and P_I defined by

$$P_0\,w = w_0, \quad P_I\,w = w_I \qquad (37)$$

are in general not Hermitian. The invariance of W_0 and W_I under M can be expressed in terms of the projections P_0 and P_I:

$$M\,P_0 = P_0\,M\,P_0, \quad M\,P_I = P_I\,M\,P_I, \qquad (38)$$

or equivalently

$$Q(t)\,P_0 = P_0\,Q(t)\,P_0, \quad Q(t)\,P_I = P_I\,Q(t)\,P_I. \qquad (39)$$

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[1] See e.g. [Halmos, 1958 section 58.]

The semi-group $Q(t)$ can thus be written as a direct sum of two semi-groups

$$Q(t) = Q(t)\,P_0 + Q(t)\,P_I = Q_0(t) + Q_I(t), \quad Q_0(t_1)\,Q_I(t_2) = Q_I(t_2)\,Q_0(t_1) = 0. \tag{40}$$

The processes determined by $Q_0(t)$ are strictly irreversible

$$\lim_{t\to\infty} Q_0(t) = 0 \tag{41}$$

and give rise to maximal entropy production

$$Q_0(0)^*\,s\,Q_0(0) = P_0^*\,s\,P_0, \; \lim_{t\to\infty} Q_0(t)^*\,s\,Q_0(t) = 0. \tag{42}$$

The processes determined by $Q_I(t)$ on the other hand are strictly reversible, and give rise to no entropy production

$$Q_I(t)^*\,s\,Q_I(t) = P_I^*\,s\,P_I = P_I^*\,s(\infty)\,P_I, \tag{43}$$

and wee see that on W_I the semi-group $Q(t)$ is equivalent within a similarity transformation to a group of unitary transformations

$$s_I^{\frac{1}{2}}\,Q_I(t)\,s_I^{-\frac{1}{2}} \text{ with } s_I = P_I^*\,s\,P_I, \; s_I^{-\frac{1}{2}}\,s_I^{\frac{1}{2}} = P_I. \tag{44}$$

The operators (44), forming a group of unitary transformations in W_I, have a spectral resolution of the form

$$s_I^{\frac{1}{2}}\,Q_I(t)\,s_I^{-\frac{1}{2}} = \sum_{\lambda'} \exp\{i\,\lambda'\,t\}\,E_{\lambda'},$$

where the summation goes over the eigenvalues of the infinitesimal generator of (44), that is over the eigenvalues of $M\,P_I$. The operators $E_{\lambda'}$ are mutually orthogonal projections forming a resolution of the identity in W_I, that is of P_I. Hence they have the properties

$$\sum_{\lambda'} E_{\lambda'} = P_I, \; E_{\lambda'}\,E_{\lambda''} = \begin{matrix} E_{\lambda'} \; (\lambda' = \lambda'') \\ 0 \quad (\lambda' \neq \lambda'') \end{matrix}, \; E_{\lambda'}^*\,P_I = P_I^*\,E_{\lambda'}. \tag{45}$$

Hence we obtain a spectral resolution of $Q_I(t)$ of the form

$$Q_I(t) = \sum_{\lambda'} \exp\{i\,\lambda'\,t\}\,s_I^{-\frac{1}{2}}\,E_{\lambda'}\,s_{I}^{\frac{1}{2}}, \tag{46}$$

and here $s_I^{-\frac{1}{2}}\,E_{\lambda'}\,s_I^{\frac{1}{2}}$ is the projection into the subspaces V_j corresponding to the eigenvalue $\mu_j = i\,\lambda'$ of M in the direct decomposition of V determined by that operator.

We note that the condition (26 a) on M is transformed into itself if M is replaced by M^* and s by s^{-1}. Thus the semi-group $Q(t)^*$ is related to $d = s^{-1}$ in the same way as $Q(t)$ is related to s. In particular we find that

$$d(t) = Q(t)\,d\,Q(t)^* \tag{46}$$

decreases monotonically with increasing t to a limit

$$\lim_{t\to\infty} d(t) = d(\infty) \tag{47}$$

which is a non negative operator bounded by d. The eigenvalues of M^* are the complex conjugate of the eigenvalues of M and have the same multiplicities. It is thus evident that

$$\text{Rank } s(\infty) = \text{Rank } d(\infty). \tag{48}$$

It follows that $s(\infty)$ and $d(\infty)$ vanish together and in that case $Q(t)$ can determine only strictly irreversible processes. If on the other hand the rank of the operators is equal to m, the number of dimensions of V, we have necessarily $s(\infty) = s$ and $d(\infty) = d = s^{-1}$, and the processes determined by $Q(t)$ are strictly reversible. We shall see later that these properties of the semi-group $Q(t)^*$ are of great value for the statistical interpretation of the linear theory of irreversible processes.

So far we have only taken into account the property (26 a) of M. We shall now consider the other conditions. The effect of the reality condition (26 b) is of course the invariance of the spectrum of M under complex conjugation. Further, if V_j is the subspace of V which corresponds to the eigenvalue μ_j of M, the subspace CV_j corresponds to the eigenvalue $\bar{\mu}_j$. M and M^* have the same spectrum.

According to Onsager's relations (26 c) M and its Hermitian adjoint are related by a similarity transformation. Thus if V_j is the subspace of V corresponding to the eigenvalue μ_j of M, $(sT)\,V_j$ is the subspace corresponding to the eigenvalue μ_j of M^*. Comparing (27) and (46) we find that $s(t)$ and $d(t)$ are related by a non singular transformation

$$(s\,T)\,d(t)\,(s\,T) = s(t). \tag{49}$$

Strict reversibility of all processes determined by $Q(t)$ is equivalent to the condition

$$M^*\,s + s\,M = 0. \tag{50}$$

Combining this with Onsager's relations (26 c) we find

$$T\,M\,T = -M. \tag{51}$$

Denoting by $v(t, v_0) \equiv Q(t)\,v_0$ that integral of the phenomenological equations which corresponds to the initial state v_0 at $t=0$, we obtain from (51) the relation

$$T\,v(t, v_0) = v(-t, T\,v_0). \tag{52}$$

The effect of T applied to a strictly reversible process is thus really a reversion of the direction of motion.

If on the other hand we assume strict reversibility (50) and the reality condition (26 b) it is always possible to define an operator T which is involutory and has the property (51). To see this we note that according to (50) the operator $s^{\frac{1}{2}}\,M\,s^{\frac{1}{2}}$ is anti Hermitian. Further it is real, that is it commutes with C. Hence its spectral resolution is of the form

$$s^{\frac{1}{2}}\, M\, s^{\frac{1}{2}} = \sum_{\lambda} i\,\lambda\, P_{\lambda} \tag{53}$$

with orthogonal projections P_{λ} corresponding to the eigenvalues λ. With P_{λ} also $P_{-\lambda}$ occurs in the expansion (53). The corresponding subspaces have the same number of dimensions and hence it is always possible to find a transformation $\tilde{T}$ which is involutory and maps $P_{\lambda}V$ on $P_{-\lambda}V$:

$$\tilde{T}\,\tilde{T} = 1, \qquad \tilde{T}\, P_{\lambda} = P_{-\lambda}\, \tilde{T}. \tag{54}$$

From (54) and (53) it follows that

$$\tilde{T}\, s^{\frac{1}{2}}\, M\, s^{\frac{1}{2}}\, \tilde{T} = - s^{\frac{1}{2}}\, M\, s^{\frac{1}{2}}. \tag{55}$$

We may take $T = s^{-\frac{1}{2}}\, \tilde{T}\, s^{\frac{1}{2}}$ in order to satisfy (50).

We shall now discuss the question whether is possible to introduce an operator T satisfying (26 c) and being involutory if only the conditions (26 a and b) are assumed to be satisfied. To facilitate the discussion we shall assume that the representative space V has been chosen so that the entropy operator is represented by the unit operator. There is obviously no restriction in this choice of representation. We note that in this representation a possible time reversal operator T will have the properties

$$T = T^{*} = T^{-1}. \tag{56}$$

Further $L = M$, and if this operator is decomposed into its Hermitian and its anti Hermitian parts

$$L = L_H + L_A \tag{57}$$

the Onsager relations take the form

$$T\, L_H\, T = L_H = L_H^{*}, \qquad T\, L_A\, T = -L_A = L_A^{*}. \tag{58}$$

Both L_H and L_A are real, that is they commute with C. The first relation in (58) shows that T and L_H commute. Hence we may choose a basis in V which diagonalizes them both. From (56) it is seen that the possible eigenvalues of T are 1 and -1. The condition (26 a) is equivalent to the statement that the eigenvalues of L_H are non negative, and imposes no restriction on L_A. The possibility of introducing a time reversal operator (56) is thus determined by the form of L_A. Let $|1), \ldots, |m)$ be an orthonormal basis in V which diagonalizes L_H. According to condition (26 b) the matrix elements $(\mu|L_A|\nu)$ of L_A are real

$$\overline{(\mu|L_A|\nu)} = -(\nu|L_A|\mu) = (\mu|L_A|\nu). \tag{59}$$

The only possible form of a time reversal operator T is

$$T = \sum_{\mu=1}^{\mu=m} |\mu)\, \tau_{\mu}\, (\mu| \qquad (\tau_{\mu}^{2} = 1). \tag{60}$$

In order to satisfy the condition (58) we must have

$$\tau_\mu \tau_\nu (\mu | L_A | \nu) = -(\mu | L_A | \nu). \tag{61}$$

It can be seen immediately from (61) that it is always possible to find an operator T with the required properties if the dimensionality m of V is smaller than 3. But for $m \geqslant 3$ this is in general not possible and the relation (58) is a real restriction of the form of L.

Finally the condition (26 d) is equivalent to the statement that 0 is not an eigenvalue of M. This concludes the discussion of the conditions (26) which we have imposed on M.

4. Open system. Dissipation functions

In paragraph 2 we have considered a closed adiabatically insulated system under fixed external conditions. If the phenomenological equations which determine the time development of the state of the system are of the strictly irreversible type the system approaches asymptotically the equilibrium state determined by the external conditions. This approach is characterized by the monotonic variation of a dissipation function, which is identical with the first non vanishing term in the Taylor expansion of the entropy function in powers of the thermodynamic coordinates. We shall now consider the same system under conditions which are such that some of the thermodynamic forces have prescribed values

$$\xi_1(t) = \mathring{\xi}_1(t), \ldots, \xi_l(t) = \mathring{\xi}_l(t) \qquad (0 \leq l \leq m). \tag{62}$$

It is assumed that the state of the system can still be characterized by the m thermodynamic coordinates (2) and that the time development is determined by the equations

$$\frac{d}{dt} \alpha^{\mu''}(t) = L^{\mu''\nu} \xi_\nu(t) \qquad (\nu = 1, \ldots, m;\ \mu'' = l+1, \ldots, m) \tag{63}$$

for the "free" thermodynamic coordinates.[1] In general the constraints (62) will prevent the system from being closed and adiabatically insulated. If in particular the constraints (62) are independent of the time the system may eventually reach a steady state. It is easily seen that in this case the approach to the steady state may be characterized by the monotonic behaviour of a dissipation function, analogous to the entropy function for the closed adiabatically insulated system.

For the discussion of the equations (62), (63) it is convenient to use the representation described in paragraph 3. We introduce the, in general nonorthogonal, projections P_1 and P_{11} in V defined in terms of the basis $u^1, \ldots, u^m$

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[1] In the following primed indices can take the values $1, \ldots, l$, doubly primed indices the values $l+1, \ldots, m$ and unprimed indices the values $1, \ldots, m$.

$$P_1\, u^{\mu'} = u^{\mu'} \qquad (\mu' = 1, \ldots, l) \tag{64}$$

$$P_1\, u^{\mu''} = 0 \qquad (\mu'' = l+1, \ldots, m)$$

$$P_{11} = 1 - P_1.$$

Writing
$$\alpha(t) = \alpha^{\mu}(t)\, u_{\mu}, \quad \xi(t) = \xi_{\mu}(t)\, u^{\mu}, \tag{65}$$

we may express (62) and (63) in the form

$$P_1\, \xi(t) = \mathring{\xi}(t), \qquad P^*_{11} \frac{d}{dt} \alpha(t) = P^*_{11} L \xi. \tag{66}$$

In order to obtain an equation for the time development of the state we use the identity

$$P^*_{11} s^{-1} P_{11}\, \xi(t) = -\{P^*_{11} s^{-1} P_1\, \mathring{\xi}(t) + P^*_{11}\, \alpha(t)\}, \tag{67}$$

to eliminate $P_{11}\,\xi(t)$ from the second relation in (66). We note the existence of a unique operator s_{11} satisfying

$$s_{11} P^*_{11} s^{-1} P_{11} = P_{11} \tag{68}$$

$$s_{11} P^*_1 = 0.$$

It follows from (68) that s_{11} is non negative. Hence (67) has the unique solution

$$P_{11}\, \xi(t) = -s_{11}\, [P^*_{11} s^{-1} P_1\, \mathring{\xi}(t) + P^*_{11}\, \alpha(t)] = -s_{11}\, [s^{-1}\, \mathring{\xi}(t) + \alpha(t)], \tag{69}$$

and we obtain from (66) the equation

$$\frac{d}{dt} P^*_{11}\, \alpha(t) = -P^*_{11} L s_{11}\, \alpha(t) + P^*_{11} L\, [\mathring{\xi}(t) - s_{11} s^{-1}\, \mathring{\xi}(t)]. \tag{70}$$

Introducing

$$M_{11} = P^*_{11} L S_{11}, \;\; M_{11}\, \eta(t) = -P^*_{11} L\, [\mathring{\xi}(t) - s_{11} s^{-1}\, \mathring{\xi}(t)] \tag{71}$$

we obtain the equation (70) in the form

$$\frac{d}{dt} [P^*_{11}\, \alpha(t)] = -M_{11}\, [P^*_{11}\, \alpha(t) + P^*_{11}\, \eta(t)]. \tag{72}$$

From the non negativity of $L + L^*$ follows that of

$$P^*_{11} (L + L^*) P_{11} = P^*_{11} L P_{11} + [P^*_{11} L P_{11}]^*,$$

and hence
$$s_{11} M_{11} + M^*_{11} s_{11} \geqslant 0. \tag{73}$$

That is, we find that M_{11} and s_{11} are related in the same way as M and s.

Both s and s_{11} are non negative operators, but s_{11} is in general singular. It is now evident that

$$s_{11}(t) = \exp\{-t\, M_{11}^*\}\, s_{11} \exp\{-t\, M_{11}\} \tag{74}$$

decreases monotonically from the value s_{11} at $t=0$ to some non negative limit $s_{11}(\infty)$. The properties of $s_{11}(\infty)$ are determined by the spectrum of M_{11}. In particular we note that if M can give rise only to processes of the strictly irreversible type we have $s_{11}(\infty)=0$.

The formal integral of the equation (72) is

$$P_{11}^*\, \alpha(t)_{t_0} = \exp\{-(t-t_0)\, M_{11}\}\, P_{11}^*\, \alpha(t_0) - \int_{t_0}^{t} \exp\{-(t-t')\, M_{11}\}\, M_{11}\, P_{11}^*\, \eta(t')\, dt', \tag{75}$$

the first term on the right hand side representing the changes which are due to processes inside the system and the second term representing the changes due to the external constraints. If in particular $s_{11}(\infty)=0$, that is if the changes taking place inside the system are strictly irreversible, and if $\eta(t)$ is sufficiently wellbehaved as a function of t, for instance if $\|\eta(t)\| \leqslant C < \infty$ for all values of t, we can let $t_0 \to -\infty$ in equation (75) and obtain the "long time" solution of (72)

$$P_{11}^*\, \alpha(t)_\infty = -\int_0^\infty \exp\{-t'\, M_{11}\}\, M_{11}\, P_{11}^*\, \eta(t-t')\, dt' \tag{76}$$

that is the solution which any solution of (72) approaches asymptotically. We want to characterize the approach of an arbitrary solution $\alpha(t)_0$ determined by e.g. $\alpha(0)$ to the "long time" solution, which is independent of $\alpha(0)$, by the monotonic decrease of a dissipation function. The difference between the two solutions (75) and (76) is

$$P_{11}^*\, [\alpha(t)_0 - \alpha(t)_\infty] = \exp\{-t\, M_{11}\}\, [\alpha(0) - \int_{-\infty}^{0} \exp\{t'\, M_{11}\}\, M_{11}\, P_{11}^*\, \eta(t')\, dt'] \tag{77}$$

and

$$\| s_{11}^{\frac{1}{2}}\, P_{11}^*\, [\alpha(t)_0 - \alpha(t)_\infty] \|^2 = \| s_{11}(t)^{\frac{1}{2}}\, [\alpha(0) - \int_{-\infty}^{0} \exp\{t'\, M_{11}\}\, M_{11}\, P_{11}^*\, \eta(t')\, dt'] \|^2 \tag{78}$$

decreases monotonically to zero. Hence (78) which evidently is a unique function of the state $\alpha(t)$ of the system, may be used to characterize the approach towards the "long time" behaviour, which is only dependent on the external constraints. This dependence is causal in the sense that the state at the time t is determined by the values of the external parameters at times prior to t. If in particular the external constraints are time independent, $\eta(t) = \eta$, (78) can be written

$$\| s_{11}^{\frac{1}{2}}\, [\alpha(t)_0 - P_1^*\, \eta] \|^2 \tag{79}$$

and the steady state is given by

$$P_{11}^*\, \alpha_{\text{steady}} = -P_{11}^*\, \eta.$$

The existence of the dissipation function (79) may be considered, at least partially, as an affirmative answer to a wellknown question raised by the Ehrenfests [Ehrenfest, 1911 p. 82] about the possibility of characterizing the steady state by the minimum of some function which could be considered as a generalization of Boltzmann's H-function.

It is interesting to compare the characterization of the steady state discussed above with Prigogine's theorem of minimum entropy production [Prigogine, 1947]. To obtain Prigogine's theorem we observe that a steady state, given the constraint $P_1 \xi = \mathring{\xi}$ is characterized by

$$\frac{d}{dt} P_{11}^* \alpha_{\text{steady}} = P_{11}^* L \xi_{\text{steady}} = P_{11}^* L P_{11} \xi_{\text{steady}} + P_{11}^* L P_1 \mathring{\xi} = 0. \tag{80}$$

Assuming that this equation has at least one solution $P_{11} \xi_{\text{steady}}$, and this will always be the case if L is non singular we may describe an arbitrary state by

$$\xi = \xi_{\text{steady}} + \Delta \xi, \quad P_{11} \Delta \xi = \Delta \xi. \tag{81}$$

Consider now the expression $(\xi | L | \xi)$ and apply (80).

$$(\xi | L | \xi) = (\xi_{\text{steady}} | L | \xi_{\text{steady}}) + (\Delta \xi | L | \Delta \xi). \tag{82}$$

In the case that L is Hermitian (82) represents the entropy production in the state determined by ξ. The quadratic form is non negative and evidently takes its minimum value for $\Delta \xi = 0$. Thus, if L is Hermitian and non singular there will always exist a unique steady state determined as the state of minimum entropy production. This is the content of Prigogine's theorem. It is obvious that under the conditions of Prigogine's theorem the system will reach its steady state in the course of time.

To see that the decrease of the entropy production to its stationary value is monotonic we write the integral of the equations (66) in terms of the thermodynamic forces, observing that the constraints are independent of time,

$$\begin{aligned} \xi(t) = \exp\{-t[s_{11} P_{11}^* L P_{11}]\} [P_{11} \xi(0) + (s_{11} P_{11}^* L P_{11})^{-1} s_{11} P_{11}^* L \mathring{\xi}] - \\ - (s_{11} P_{11}^* L P_{11})^{-1} s_{11} P_{11}^* L \mathring{\xi} + \mathring{\xi} \equiv \Delta \xi(t) + \xi_{\text{steady}}. \end{aligned} \tag{83}$$

Here $(s_{11} P_{11}^* L P_{11})^{-1}$ is defined by

$$\begin{aligned} (s_{11} P_{11}^* L P_{11}) (s_{11} P_{11}^* L P_{11})^{-1} = P_{11} \\ P_1 (s_{11} P_{11}^* L P_{11})^{-1} = 0. \end{aligned} \tag{84}$$

Let A be an arbitrary operator in V and consider the derivative of the matrix element $(\Delta \xi(t) | A | \Delta \xi(t)) \equiv (\Delta \xi(t) | P_{11}^* A P_{11} | \Delta \xi(t))$:

$$\begin{aligned} \frac{d}{dt} (\Delta \xi(t) | A | \Delta \xi(t)) = \\ = -(\Delta \xi(t) | P_{11}^* L P_{11} s_{11} P_{11}^* A P_{11} + P_{11}^* A P_{11} s_{11} P_{11}^* L P_{11} | \Delta \xi(t)), \end{aligned} \tag{85}$$

and this expression is non positive for every choice of $\Delta\xi(t)$ if and only if

$$(P_{11}^* L^* P_{11})\, s_{11}\, (P_{11}^* A P_{11}) + (P_{11}^* A P_{11})\, s_{11}\, (P_{11}^* L P_{11}) \geqslant 0. \tag{86}$$

We note that the solution (83) is valid under the sole assumption that $s_{11} P_{11}^* L P_{11}$ is invertible in the sense of (84). Hence it is valid whether L is Hermitian or not, whether L is of the strictly irreversible type or not. However, ξ_{steady} will be the limit of (83) only if all the processes taking place inside the system are strictly irreversible.

Assuming now with Prigogine that L is Hermitian and taking $A = L$ in (85) we find that (86) is satisfied, and comparing with (82) we find that the decrease of the entropy production is monotonic.

Another possibility of satisfying (86) is to take $A = s^{-1}$. Using the definition (68) of s_1 we find that (86) becomes

$$P_{11}^* L^* P_{11} + P_{11}^* L P_{11} = P_{11}^* (L^* + L) P_{11} \geqslant 0, \tag{87}$$

and this inequality is valid on the basis of the non negativity of $L + L^*$. Hence $(\Delta\xi\,|\,s^{-1}\,|\,\Delta\xi)$ is a dissipation function of the type required by Ehrenfest. It is easily seen that if in $(\Delta\xi\,|\,s^{-1}\,|\,\Delta\xi)$ the thermodynamic forces are expressed as functions of the thermodynamic coordinates we obtain the dissipation function (79) for the particular case of time independent constraints.

It is thus seen that the dissipation function (79) is different from Prigogine's entropy production but that the monotonic decrease of both functions is due to the same property of the phenomenological equations.

The dissipation function (79) has been defined in terms of the operator s_{11}, given by (68). We shall conclude this section with a discussion of the thermodynamic signification of this operator. We recall that the entropy operator s is defined by

$$s = -\,|\,u^\mu)\, \frac{\partial^2 S}{\partial\alpha^\mu\,\partial\alpha^\nu}(0)\, (u^\nu\,|, \tag{88}$$

where $S(\alpha)$ is the entropy function. The inverse of s can be expressed in terms of the Massieu-Planck function [Uhlhorn, 1960 a]

$$Y(\beta) = \beta_\mu \alpha^\mu + S(\alpha) \qquad \left(\beta_\mu = \frac{\partial S}{\partial\alpha^\mu}(\alpha)\right), \tag{89}$$

$$s^{-1} = |\,u_\mu)\, \frac{\partial^2 Y}{\partial\beta_\mu\,\partial\beta_\nu}(0)\, (u_\nu\,|. \tag{90}$$

Hence

$$P_{11}^*\, s^{-1}\, P_{11} = |\,u_{\mu''})\, \frac{\partial^2 Y}{\partial\beta_{\mu''}\,\partial\beta_{\nu''}}(0)\, (u_{\nu''}\,|. \tag{91}$$

Expressing s_{11} in the form

$$s_{11} = |\,u^{\mu''})\, s_{11\mu''\nu''}\, (u^{\nu''}\,|, \tag{92}$$

we find that $s_{11\lambda''\nu''} = s_{11\nu''\lambda''}$ is determined by

$$s_{11\lambda''\nu''}\, \frac{\partial^2 Y}{\partial\beta_{\nu''}\,\partial\beta_{\mu''}} = \delta_{\lambda''}^{\mu''}. \tag{93}$$

We recall that doubly primed indices take the values $l+1, \ldots, m$. Considering the generalized thermodynamic potential Y_l defined by

$$Y_l = Y_l(\beta_1, \ldots, \beta_l, \alpha^{l+1}, \ldots, \alpha^m) = \sum_{\mu'=1}^{\mu'=l} \frac{\partial S}{\partial \alpha^{\mu'}} \alpha^{\mu'} - S \tag{94}$$

we find [Uhlhorn, 1960 a, equation (53)] that

$$s_{11\lambda''\nu''} = -\frac{\partial^2 Y_l}{\partial \alpha^{\lambda''} \partial \alpha^{\nu''}} \tag{95}$$

the derivative being taken at the reference state (2). Introducing $\Delta \alpha^\mu = \alpha^\mu(t)_0 - \alpha^\mu(t)_\infty$, (77), we find that the dissipation function (78) can be written

$$-\frac{\partial^2 Y_l}{\partial \alpha^{\lambda''} \partial \alpha^{\nu''}} \Delta \alpha^{\lambda''} \Delta \alpha^{\nu''}. \tag{96}$$

Hence we have found how the dissipation function is related to the thermodynamic functions of the system. Returning to Ehrenfest's question, we compare the expression (93) with the generalized form of Boltzmann's principle [Uhlhorn, 1960 a, (71)]. We find that for time independent constraints the dissipation function (93) determines the probability distribution of the fluctuations in the stationary state.

Dissipation functions of the type discussed above can be defined for continuous systems also as far as the kinetic equations can be considered as linear, that is for systems in mechanical equilibrium, if the phenomenological coefficients are independent of the space coordinates.

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